BRIEF COMMUNICATIONS

Thermodynamics of Discharge of the Negative Electrode of a Nickel–Iron Battery

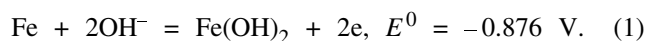## A. I. Demidov, M. S. Kokhatskaya, and B. V. Chernovets

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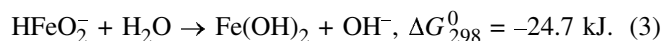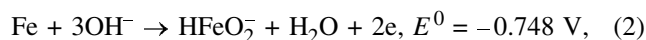
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Abstract—The standard Gibbs energies and standard potentials of reactions expected to occur in discharge of the negative electrode of a nickel–iron battery were calculated.

The following equation was suggested for describing the discharge and charging of an iron electrode in an alkaline electrolyte as far back as the beginning of the past century [1–3]:

$$\mathrm{Fe} + 2\mathrm{OH}^- = \mathrm{Fe(OH)}_2 + 2e, \quad E^0 = -0.876 \text{ V}. \quad (1)$$
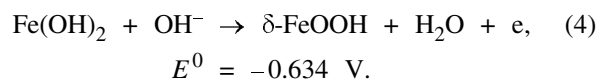
In the general form, this equation adequately reflects the initial and final states of the active paste. However, Kabanov and Leikis [4, 5] believe that process (1) occurs in two stages: first, iron is oxidized to HFeO_2^- ions and then a loose porous $\mathrm{Fe(OH)}_2$, weakly bound to the metal, precipitates from solution:

$$\mathrm{Fe} + 3\mathrm{OH}^- \rightarrow \mathrm{HFeO}_2^- + \mathrm{H}_2\mathrm{O} + 2e, \quad E^0 = -0.748 \text{ V}, \quad (2)$$

$$\mathrm{HFeO}_2^- + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{Fe(OH)}_2 + \mathrm{OH}^-, \quad \Delta G_{298}^0 = -24.7 \text{ kJ}. \quad (3)$$
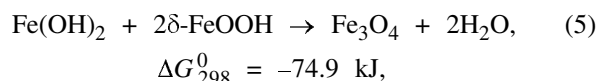
A study of anodic films on iron in alkaline solutions by the ellipsometry and chronoamperometry [6–8] made it possible to suggest the following mechanism of growth of anodic films on iron. A denser anodic film adjacent to the metal is formed via deposition of a $\mathrm{Fe(OH)}_2$ layer onto the electrode. Its growth in the course of time is limited by the velocity of migration of Fe^{2+} ions, formed in anodic polarization, under the action of the potential and concentration gradients toward the interface between the film and solution. HFeO_2^- ions are possibly formed, together with $\mathrm{Fe(OH)}_2$, in anodic polarization of iron [reaction (2)]. The near-electrode layer is supersaturated with HFeO_2^- ions and, as a result of hydrolysis, they precipitate on the electrode in the form of $\mathrm{Fe(OH)}_2$ [reaction (3)], capturing ions from the solution and forming an outer hydrated film. Further, the outer film

degrades, loses water, and, giving up OH^- ions to the diffusing Fe^{2+} ions, becomes denser.

In the case of a strong anodic polarization of the iron electrode, the following processes may occur in a solution of the hydroxide of an alkali metal [9, 10]: first anodic process, reaction (1); and the second,
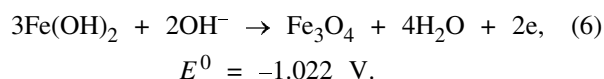
$$\mathrm{Fe(OH)}_2 + \mathrm{OH}^- \rightarrow \delta\text{-}\mathrm{FeOOH} + \mathrm{H}_2\mathrm{O} + e, \quad (4)$$
$$E^0 = -0.634 \text{ V}.$$

Teplinskaya et al. [9, 10] believe that the compound $\mathrm{Fe}_3\mathrm{O}_4$ is formed by the reaction between iron hydroxides in different oxidation states:

$$\mathrm{Fe(OH)}_2 + 2\delta\text{-}\mathrm{FeOOH} \rightarrow \mathrm{Fe}_3\mathrm{O}_4 + 2\mathrm{H}_2\mathrm{O}, \quad (5)$$
$$\Delta G_{298}^0 = -74.9 \text{ kJ},$$
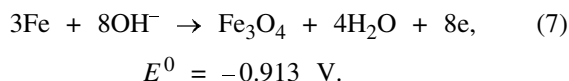
rather than by an electrochemical process.

An additional potential plateau, lying between the two known potential plateaus [reactions (1), (4)] was recorded in [11] when studying the anodic dissolution of an iron electrode at 35–55°C. An X-ray phase analysis of electrodes withdrawn from solutions after discharge at potentials of the additional plateau demonstrated that, in the electrodes, the amount of iron(II) hydroxide formed during the first anodic process decreases, and that of magnetite increases. Based on this fact, Novakovskii et al. [11] concluded that the conversion of $\mathrm{Fe(OH)}_2$ into $\mathrm{Fe}_3\mathrm{O}_4$ is described by the reaction equation

$$3\mathrm{Fe(OH)}_2 + 2\mathrm{OH}^- \rightarrow \mathrm{Fe}_3\mathrm{O}_4 + 4\mathrm{H}_2\mathrm{O} + 2e, \quad (6)$$
$$E^0 = -1.022 \text{ V}.$$

Standard Gibbs energies of various substances and ions according to [12, 13]

Substance	ΔG^0_{298}, kJ mol^{-1}	Substance	ΔG^0_{298}, kJ mol^{-1}
Fe	0	δ-FeOOH	–465.0
Fe$_3$O$_4$	–1014.2	O$_2$	0
Fe(OH)$_2$	–483.7	H$_2$O	–237.2
HFeO$_2^-$	–379.1	OH$^-$	–157.3

In the case of anodic polarization of an iron electrode within the range of the first potential plateau at 55°C, a considerable amount of magnetite is formed together with the main discharge product, Fe(OH)$_2$. Novakovskii et al. [11] believe that there occurs direct electrochemical conversion of Fe into Fe$_3$O$_4$:

$$3Fe + 8OH^- \rightarrow Fe_3O_4 + 4H_2O + 8e, \qquad (7)$$
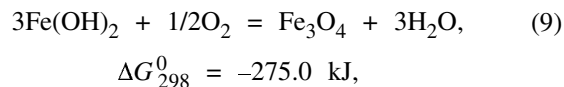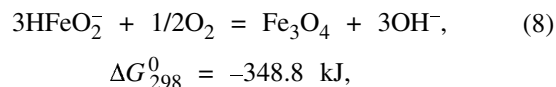
$$E^0 = -0.913 \text{ V}.$$

At elevated temperatures, the surface of separators and battery vessels is covered with a black deposit of magnetite, which indicates that magnetite may be formed in solution. The formation of magnetite is hindered on passing from LiOH solutions to those of NaOH and KOH.

In view of the wide diversity of reactions that occur in discharge of the negative electrode of a nickel–iron battery and their different orders suggested by different authors, the standard Gibbs energies and standard potentials of the above-mentioned reactions were calculated and the order of processes occurring at the electrode was refined. The calculations were based on the published standard Gibbs energies of formation [12, 13] (see table).
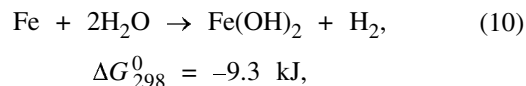
The resulting values of the standard potentials suggest the following sequence of electrochemical reactions in discharge of the negative electrode. Reaction (1) occurs at a potential of -0.876 V; reaction (2) is possible at -0.748 V to give HFeO$_2^-$ ions hydrolyzed by reaction (3); reaction (4) occurs at -0.634 V; the reaction between iron hydrates in different oxidation states [reaction (5)] yields Fe$_3$O$_4$. It should be noted that the difference of the standard potentials of reactions (4) and (1), equal to 0.242 V, is in good agreement with the abrupt potential change (0.24 V) in the discharge curve measured on a smooth iron electrode in an aqueous solution of NaOH at a current density of 2.4×10^{-5} A cm^{-2} [4].

Because the standard potential of reaction (6) is –1.022 V and significantly differs from the experimental values obtained in [11], the additional potential plateau in discharge curves at elevated temperatures is possibly due to electrochemical reaction (3) whose potential lies between the potentials of reactions (1) and (4). Magnetite is possibly formed by the reactions

$$3HFeO_2^- + 1/2O_2 = Fe_3O_4 + 3OH^-, \qquad (8)$$

$$\Delta G^0_{298} = -348.8 \text{ kJ},$$

$$3Fe(OH)_2 + 1/2O_2 = Fe_3O_4 + 3H_2O, \qquad (9)$$

$$\Delta G^0_{298} = -275.0 \text{ kJ},$$

which involve oxygen dissolved in the electrolyte. Reaction (8) also proceeds in the electrolyte bulk, which results in that a black deposit of magnetite is formed on the surface of separators and battery vessels.

Reaction (7) has a more negative standard potential than reaction (1) and, presumably, does not occur in the discharge of the iron electrode. Because iron reacts with water in accordance with the equation

$$Fe + 2H_2O \rightarrow Fe(OH)_2 + H_2, \qquad (10)$$

$$\Delta G^0_{298} = -9.3 \text{ kJ},$$

the discharge process and the subsequent charging occur across a film of iron hydroxide [reaction (1)].

The theoretical emf of the nickel–iron battery, calculated from the standard potentials of the reactions occurring at the positive [14] and negative electrodes, is 1.367 V. This value is in good agreement with the theoretical emf of 1.37 V, reported in the monograph [15].

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